Structural Physics

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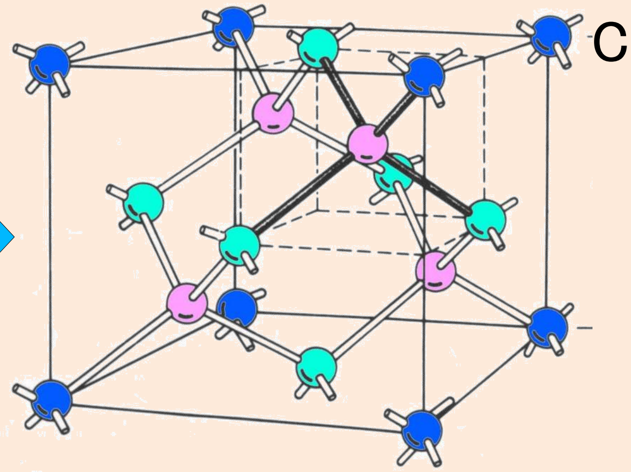
Diamond

Crystal structure



SESAME

X-ray diffraction technique

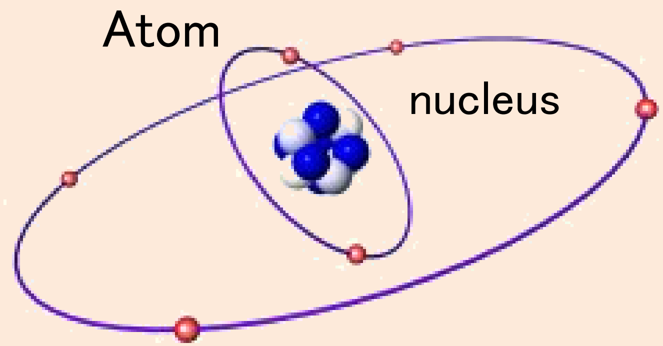
Outline of this lecture

- Structure and physical properties
- How to determine the structure

  Principle of x-ray diffraction

- Scientific applications

Structure and physical properties



Periodic table: only about 100 kinds

	1A	2A	3A	4A	5A	6A	7A	8			1B	2B	3B	4B	5B	6B	7B	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	L	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	A															
		L	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		A	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

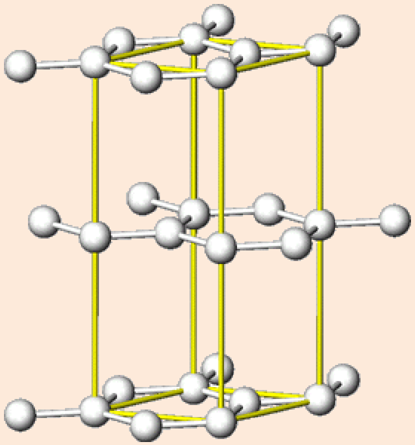
↔

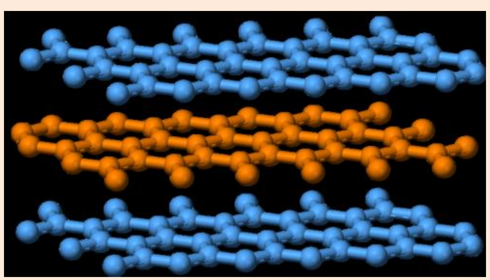
An infinite of materials
exist around us!

Arrangement of atoms (structure) is important
for the determination of the physical properties

C: atomic number 6

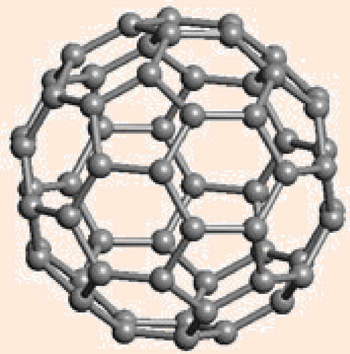
Pencil



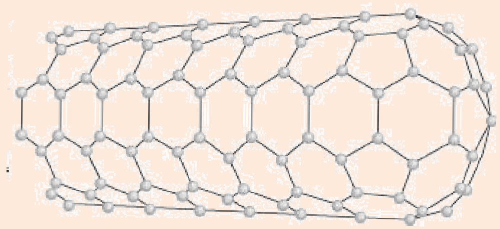


Graphite

Fullerene

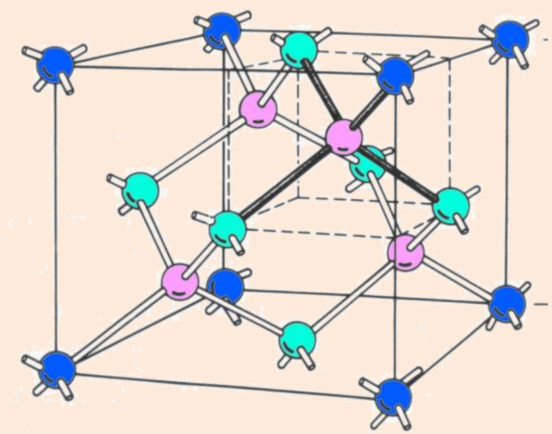


C_{60}



Nanotube

Diamond

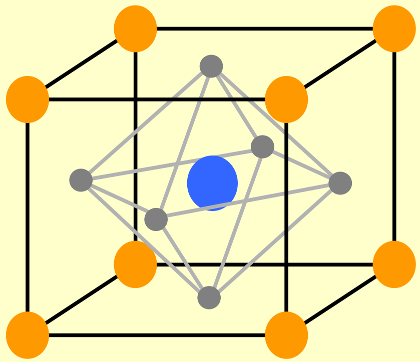


3D network

Importance of the understanding of the structure

Structure vs. Physical properties / functions

Crystal （ABO_3）

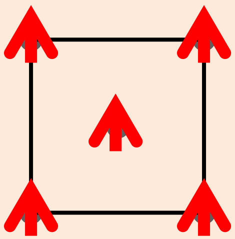


Perovskite structure

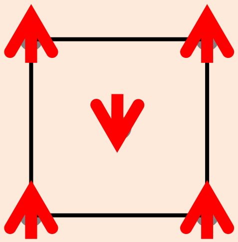
Variety of physical properties

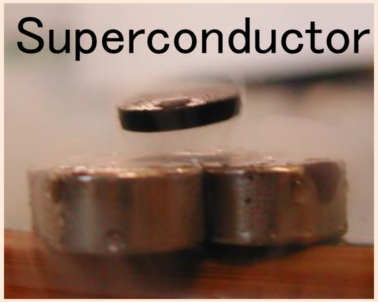
Magnetic compound

Ferro-magnetic

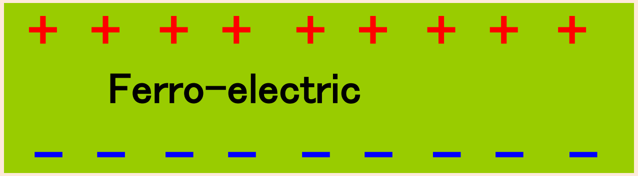


Anti-ferro-magnetic





Dielectric compound



Colossal Magneto-Resistance effect
Magneto-electric effect

Structure dominates the physical properties

Outline of this lecture

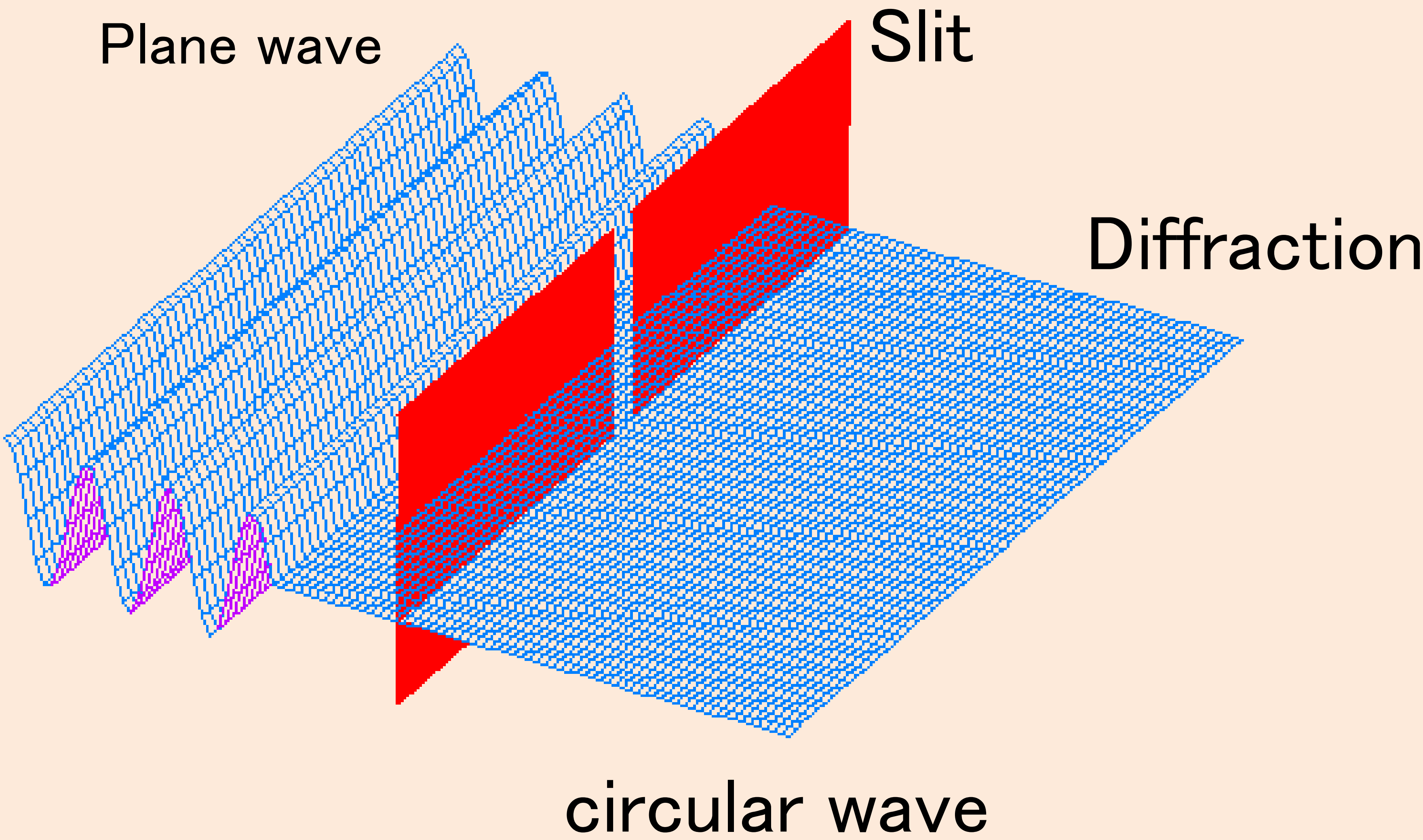
- Structure and physical properties

- How to determine the structure

  Principle of x-ray diffraction

- Scientific applications

Wave diffraction

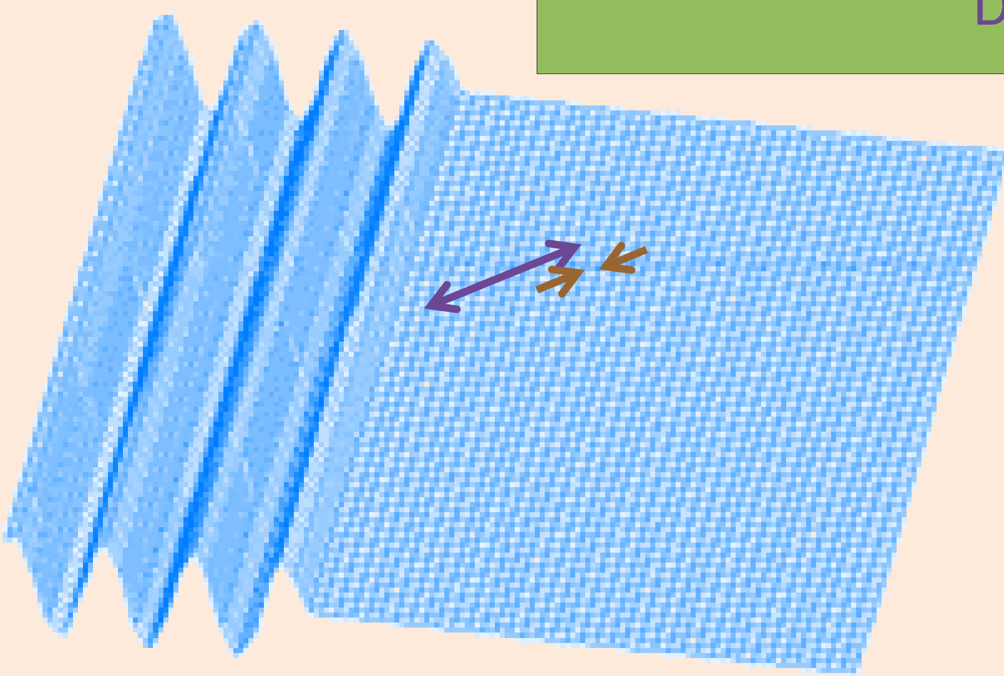


Wave Diffraction

Determination of the structure

Distance and width of slits

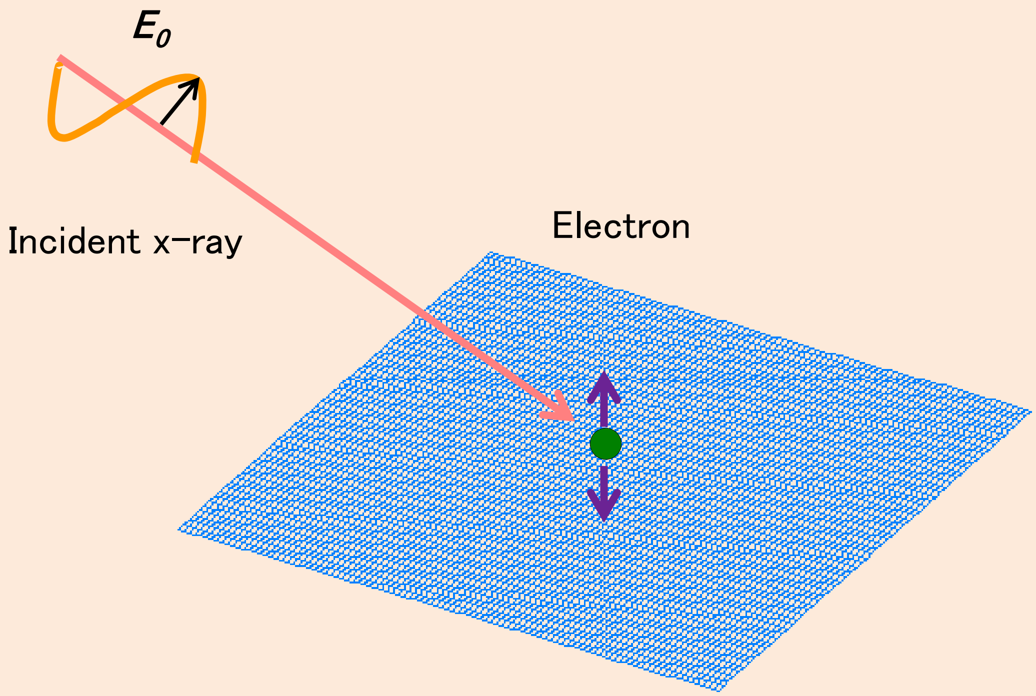
Plane wave



Interference pattern

X-ray diffraction technique

X-ray scattering of one electron



- Equation of motion of the electron

$$m\frac{d^2\boldsymbol{x}}{dt^2} = -e\boldsymbol{E}_0 \exp\{i(\boldsymbol{k}r_0 - \omega t)\}$$

$$\boldsymbol{x} = \frac{e}{m\omega^2}\boldsymbol{E}_0 \exp\{i(\boldsymbol{k}r_0 - \omega t)\}$$

simple harmonic oscillation

- Electric dipole ← $\boldsymbol{E}_0$

$$\boldsymbol{p} = -e\boldsymbol{x} = -\frac{e^2}{m\omega^2}\boldsymbol{E}_0 \exp\{i(\boldsymbol{k}r_0 - \omega t)\}$$

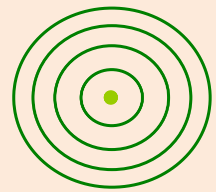
Induced emission: Spherical wave

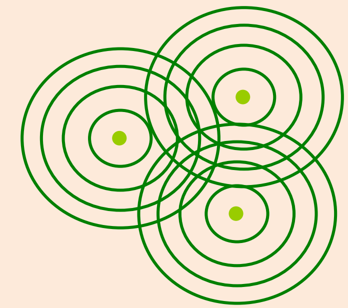
$E(r) \propto e^{ikr}$

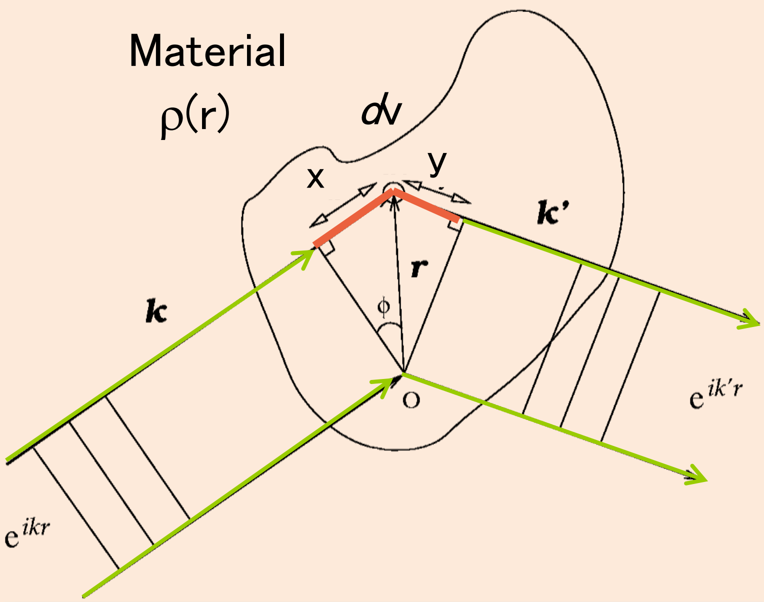
X-ray scattering from material

- Scattered x-ray from an electron

  spherical wave: $E(r) \propto e^{ikr}$







- Scattered x-ray from dv

  Optical path difference : x+y

  Phase shift = $2\pi(x+y)/\lambda = (\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}$

  $(2\pi x/\lambda = 2\pi r \sin\theta/\lambda = \mathbf{k}\cdot\mathbf{r})$

  Scattering amlitude

  → $\rho(r)\, dv\ \exp[i\,(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]$

- X-ray scattering from material

$$F(\boldsymbol{k}-\boldsymbol{k}') = \int d\boldsymbol{r}\, \rho(\boldsymbol{r}) exp[i(\boldsymbol{k}-\boldsymbol{k}')\boldsymbol{r}]$$

Structure factor: F(q) (q=k-k')

X-ray scattering intensity: $\propto |F(q)|^2$

X-ray scattering from material

$$F(\boldsymbol{q}) = \int d\boldsymbol{r}\, \rho(\boldsymbol{r}) \exp(i\boldsymbol{q}\cdot\boldsymbol{r}) \qquad \boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'$$

Fourier transform of ρ(r)

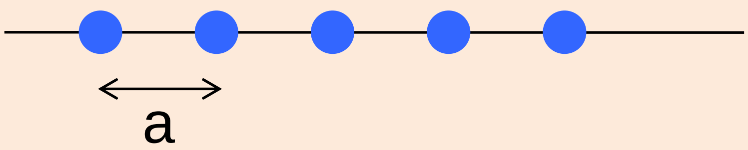
$$\rho(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \int d\boldsymbol{q} \underline{F(\boldsymbol{q})} \exp(-i\boldsymbol{q}\cdot\boldsymbol{r})$$

Electron density   Structure factor

X-ray scattering → F(q) → ρ(r),   Crystal structure

X-ray scattering from crystal

1D periodic structure



$$F(q) = \int_0^{ma} dr\, \rho(r) exp(iqr)$$

$$= \sum_{n=0}^{m-1} \exp(inqa) \cdot \int_0^{a} dR\, \rho(r) exp(iqr)$$

geometric series

$$= \frac{1-\exp(imqa)}{1-\exp(iqa)} \cdot \int_0^{a} dr\, \rho(r) exp(iqr)$$

$$= \exp(i\frac{m-1}{2}qa) \frac{\sin(mqa/2)}{\sin(qa/2)} \cdot \int_0^{a} dr\, \rho(r) exp(iqr)$$

Laue function → ρ(r) in unit cell

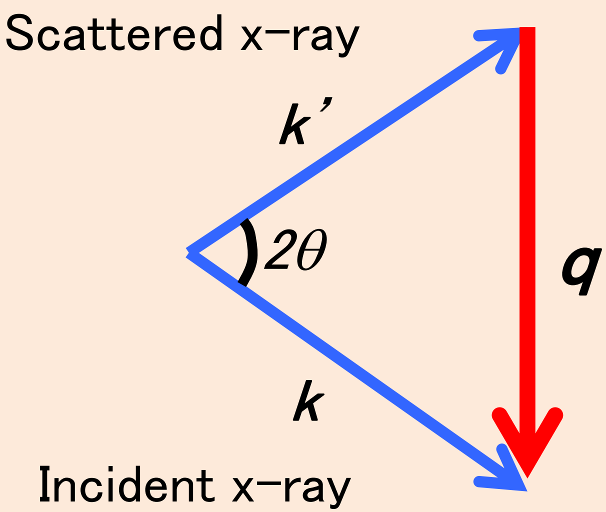
$$\begin{cases} = 0 \\ \neq 0 \quad (\text{ if } qa/2 = n\pi) \end{cases}$$

n: integer

→ **Reflection condition**

Bragg's Law

$\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'$ [F(q)]



Reflection condition

$+$

$qa/2 = n\pi$ (n: integer)

$q = 2\pi n/a$

$q = 2k \sin\theta$

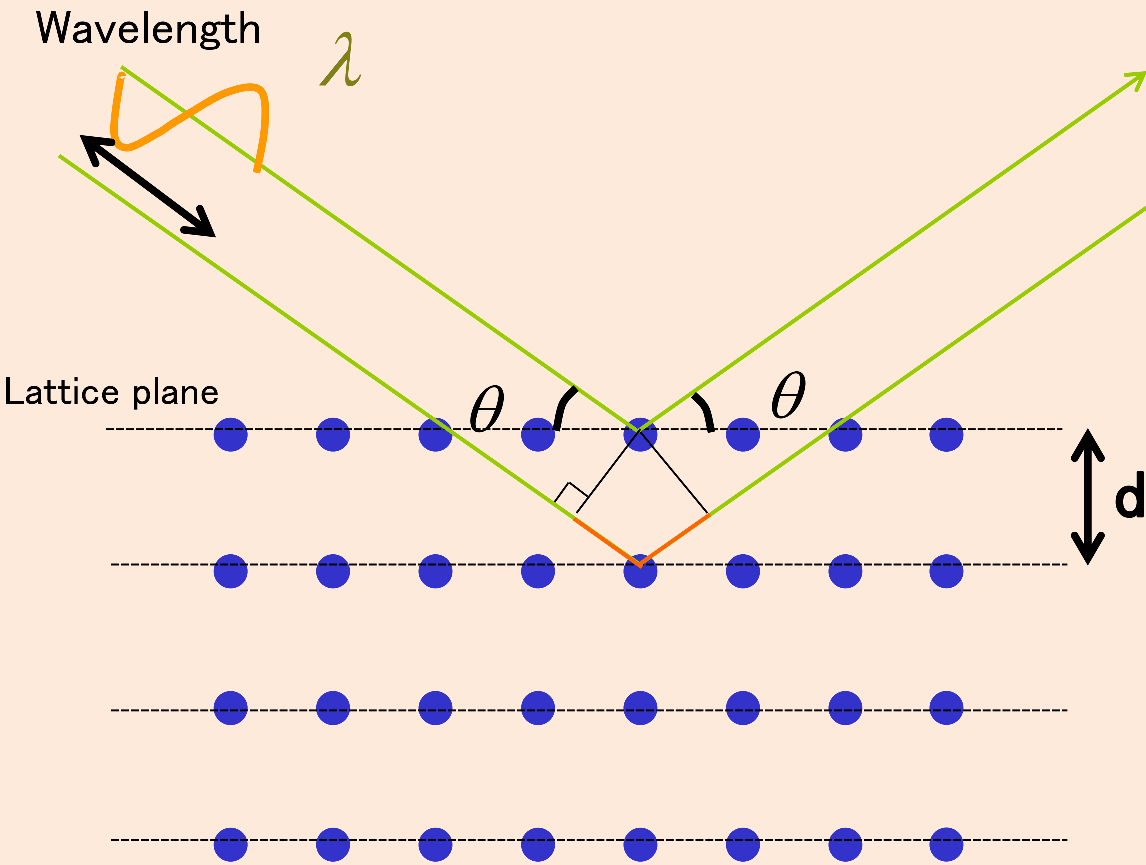
$= 2(2\pi/\lambda) \sin\theta$

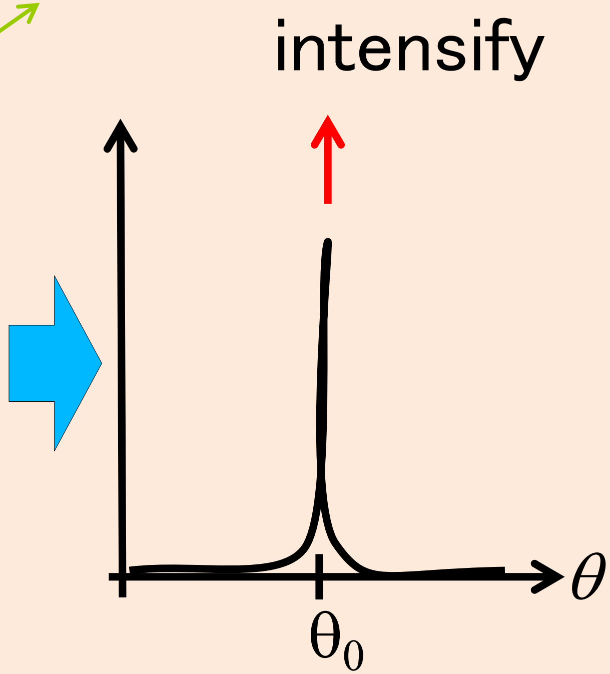
$2(2\pi/\lambda) \sin\theta = 2\pi n/a$

$$2a\sin\theta = n\lambda$$

Bragg's law

Bragg's Law → Plane distance: d



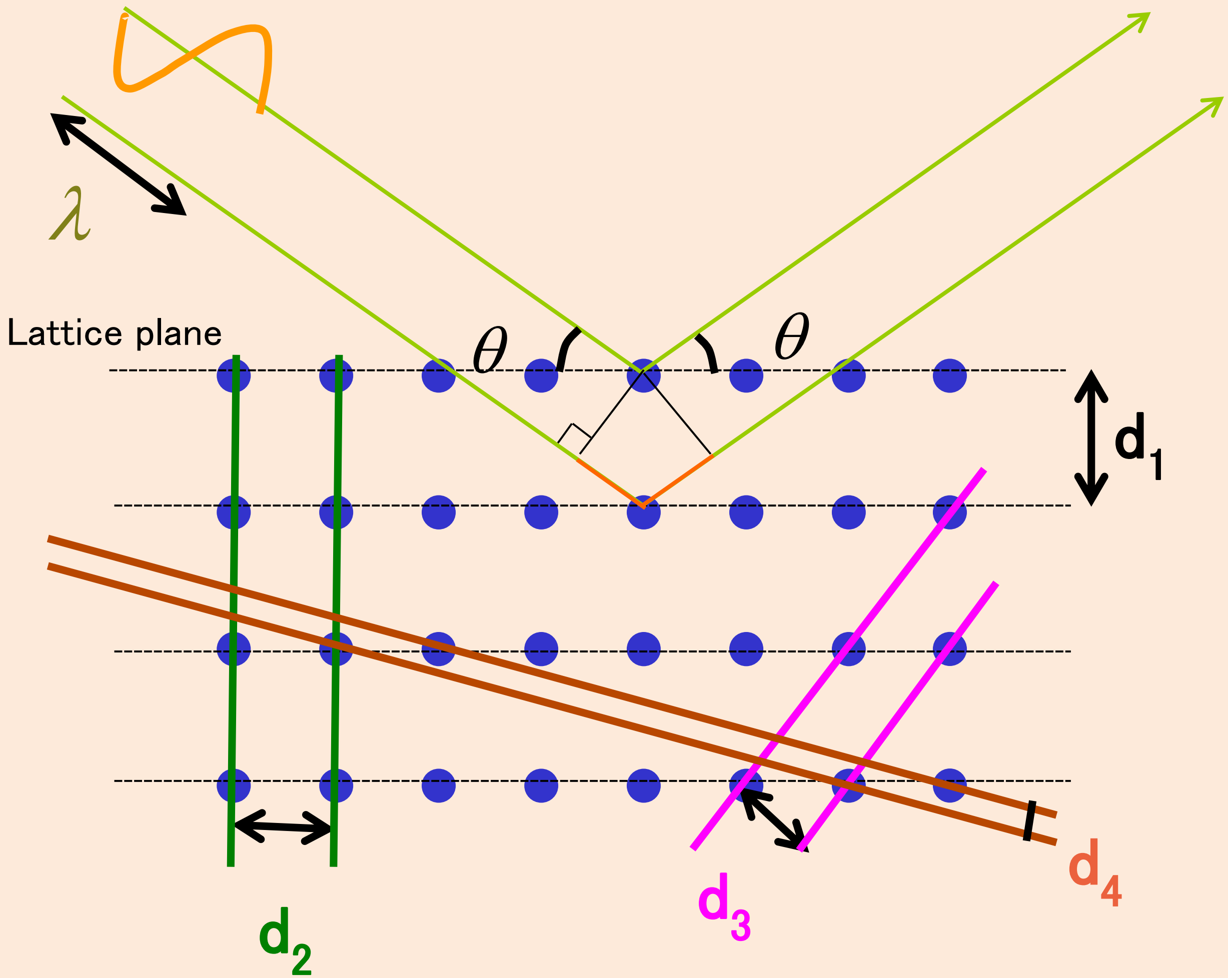


Optical path difference : $2d\sin\theta_0 = n \times \lambda$

Bragg condition

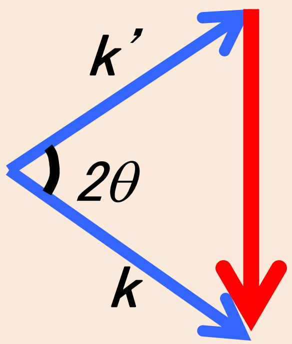
← Fourier transform of ρ(r)

Lattice planes

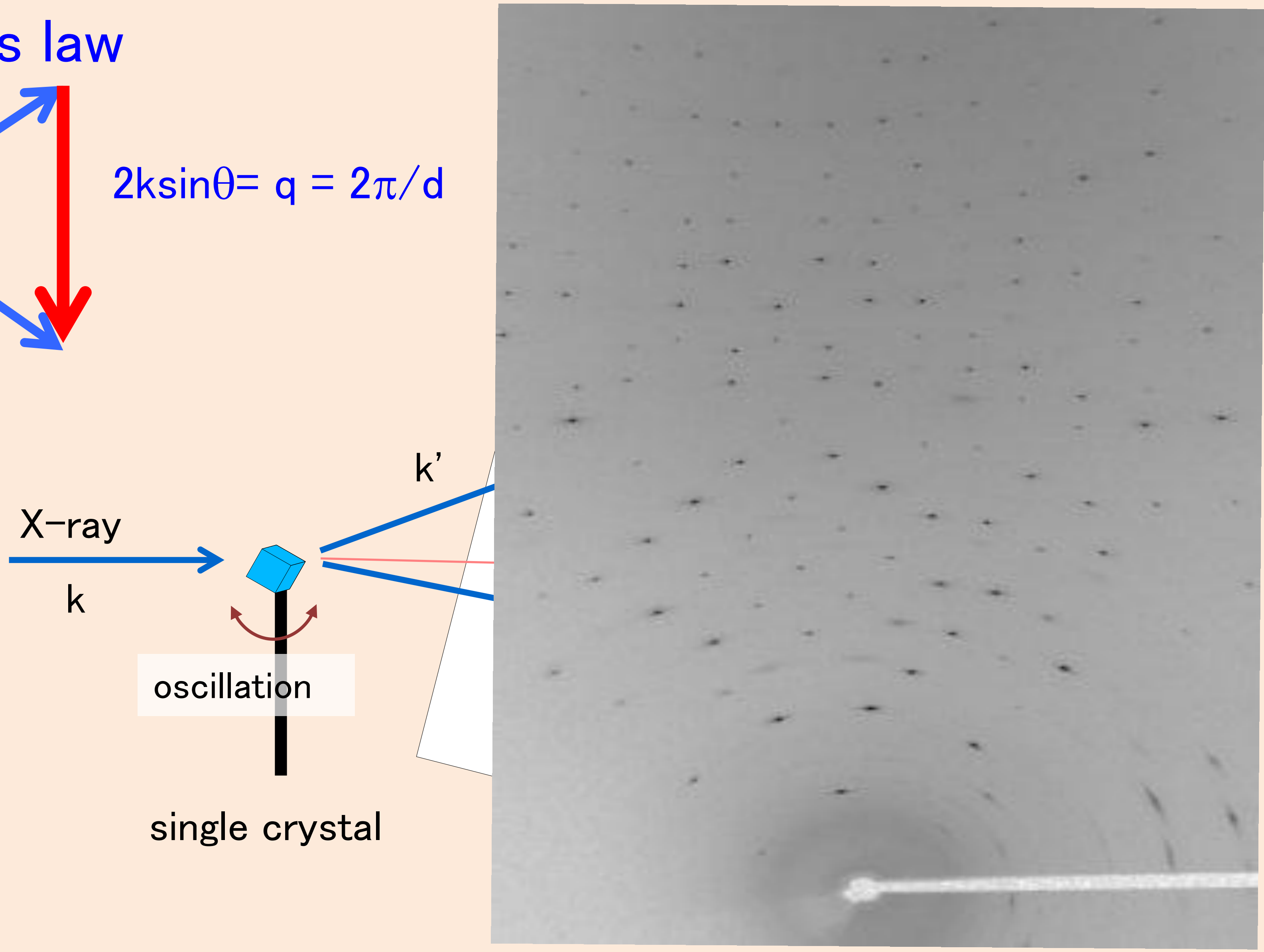


Diffraction pattern

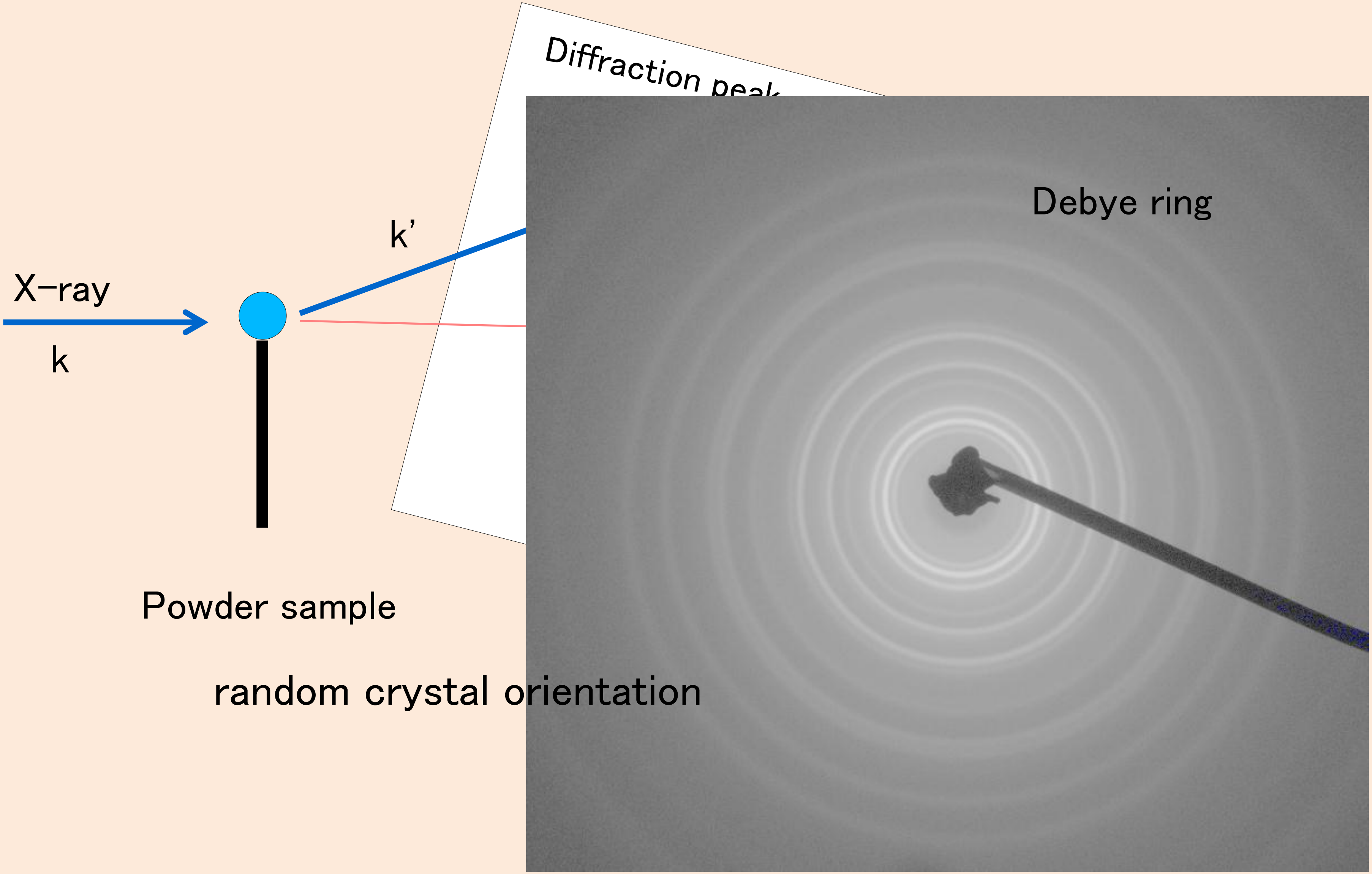
Bragg's law



$2k\sin\theta = q = 2\pi/d$



Powder x-ray diffraction



X-ray diffraction technique

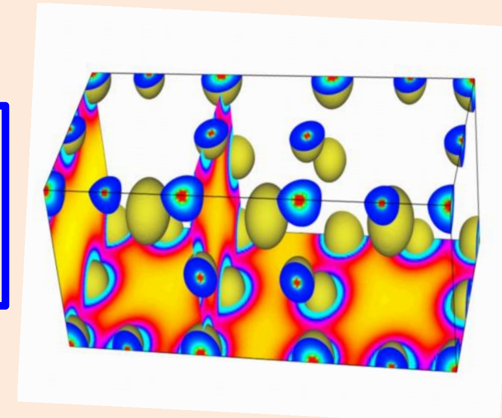
Fourier transform of ρ(r)

$$F(\boldsymbol{q}) = \int d\boldsymbol{r}\, \rho(\boldsymbol{r}) \exp(i\boldsymbol{q}\cdot\boldsymbol{r}) \qquad \boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'$$

X-ray Intensity

Electron density map in unit cell

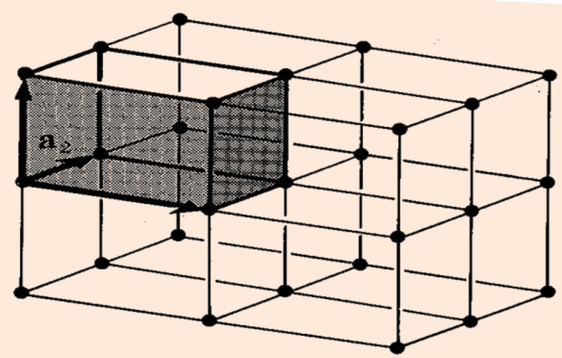
$$\rho(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \int d\boldsymbol{q} F(\boldsymbol{q}) \exp(-i\boldsymbol{q}\cdot\boldsymbol{r})$$



Crystal structure

Peak position

Bragg's Law: 2dsinθ=nλ

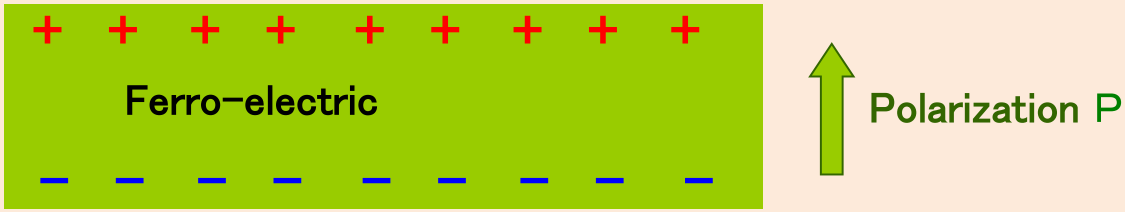


Size of unit cell

Outline of this lecture

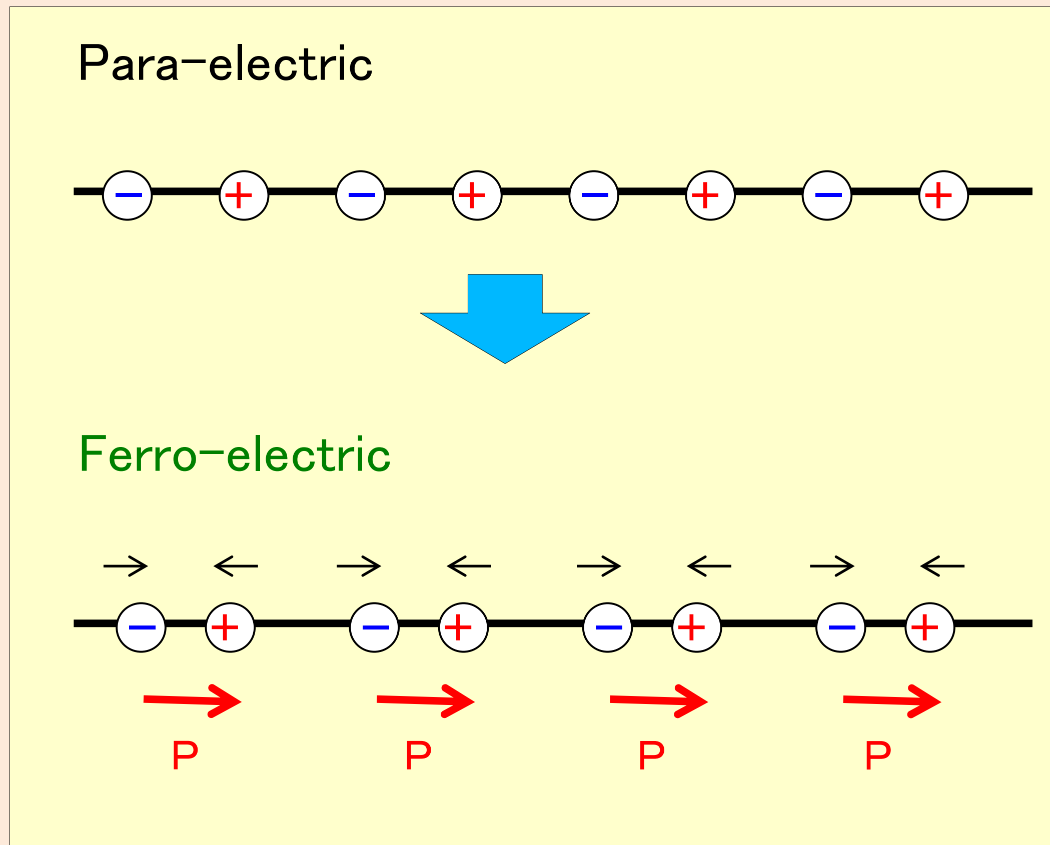
- Structure and physical properties
- How to determine the structure
  Principle of x-ray diffraction
- Scientific applications

Ferro-electric compound



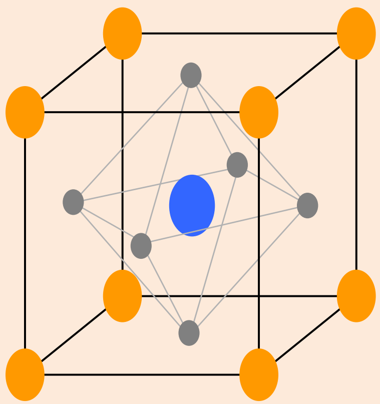
Piezoelectric element

FeRAM Memory

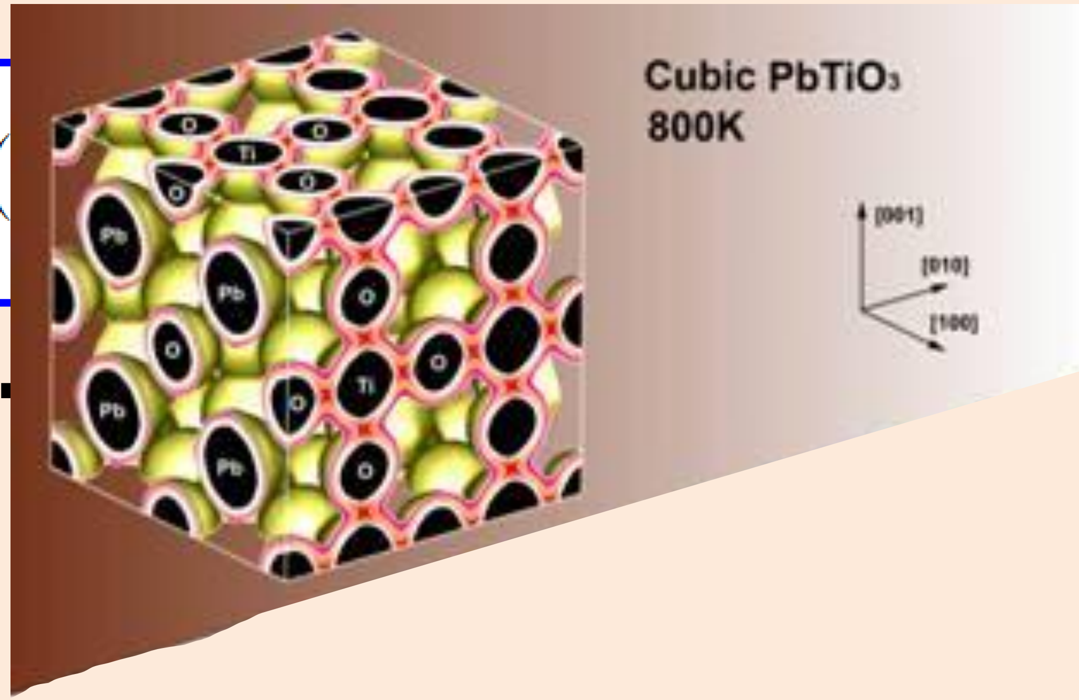


Origin of the polarization

$PbTiO_3$



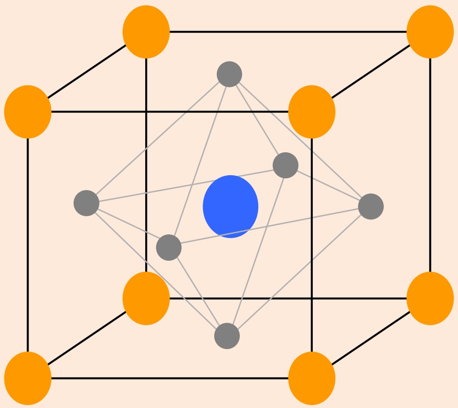
$\rho($ … $q \cdot r)$



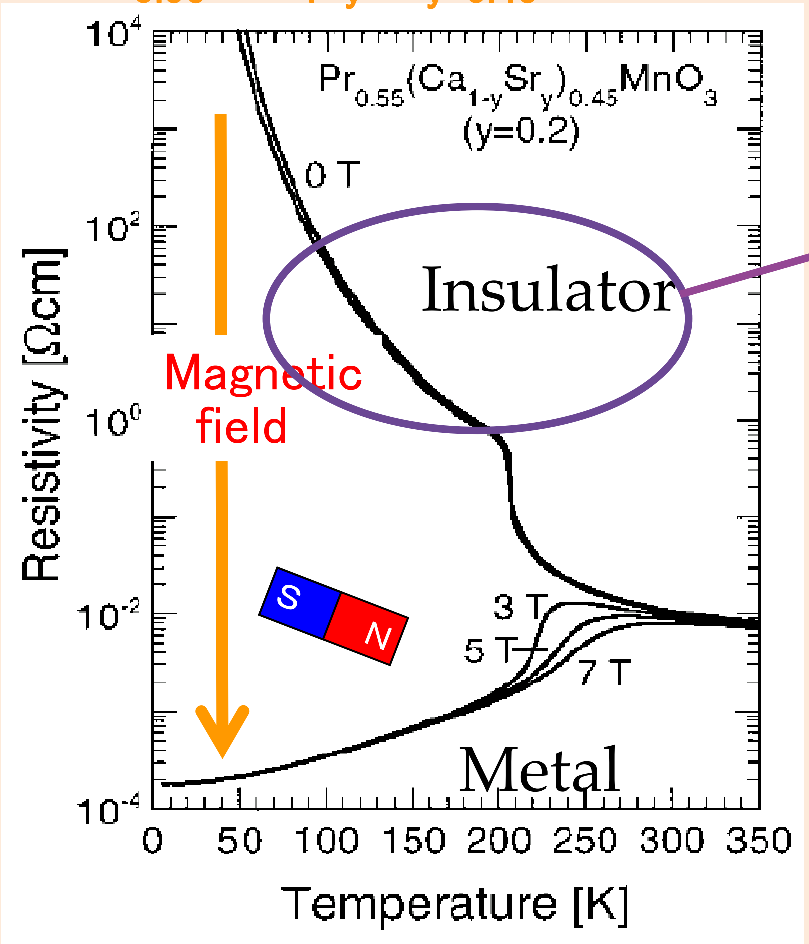
Anisotropic electron distribution!

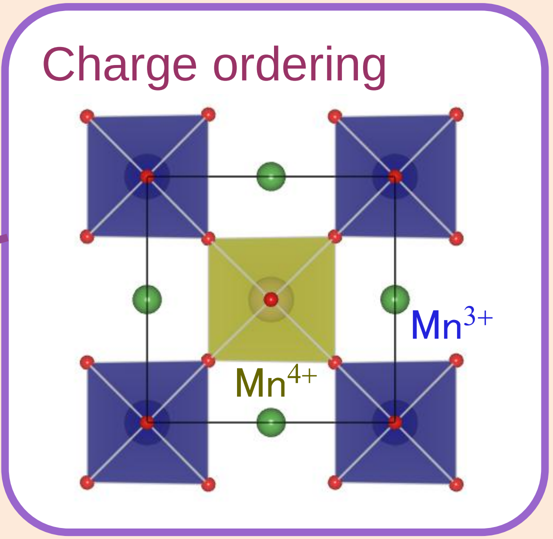
Field induced Metal-Insulator transition

Colossal magnetoresistance (CMR) effect

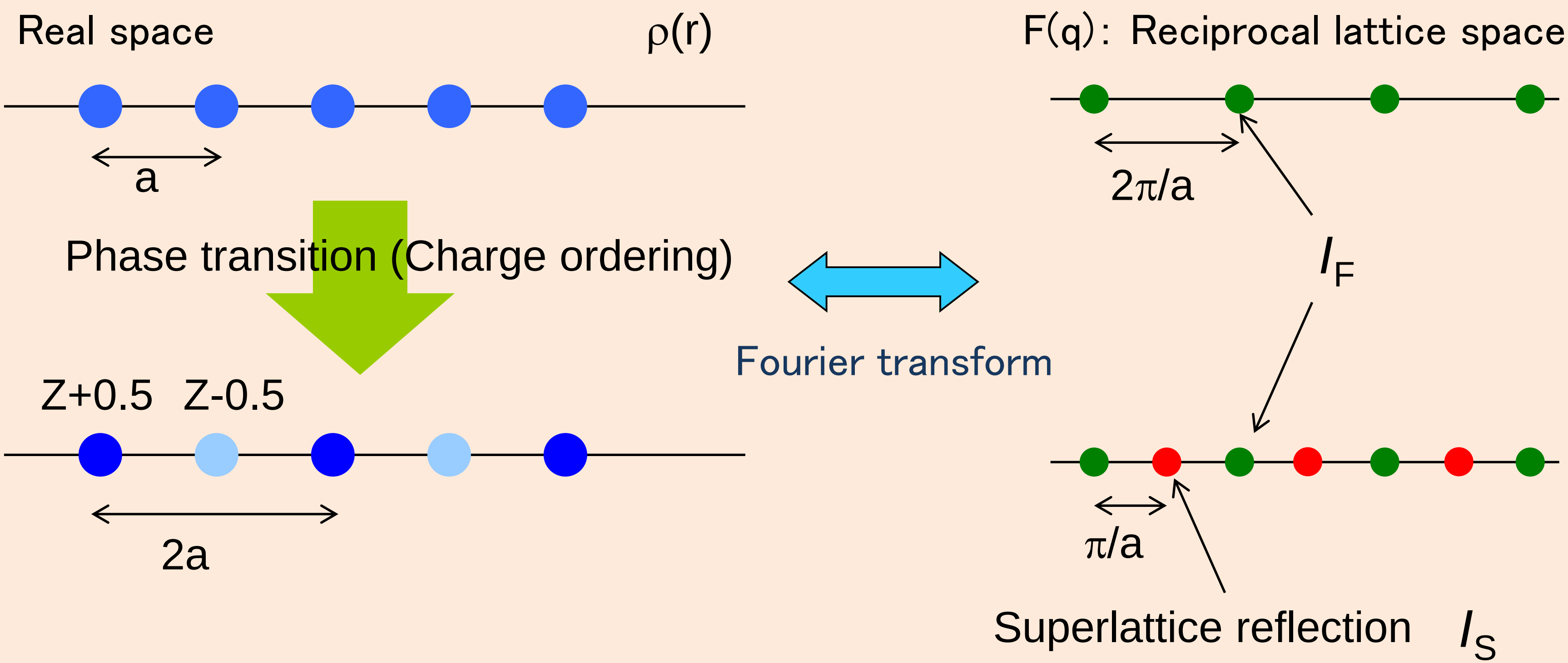


$Pr_{0.55}(Ca_{1-y}Sr_y)_{0.45}MnO_3$





Charge ordering observed by XRD



$I_F : I_S \sim 4Z^2 : 1$

I_S: reflecting the difference of one electron

To detect weak signal *Is*,

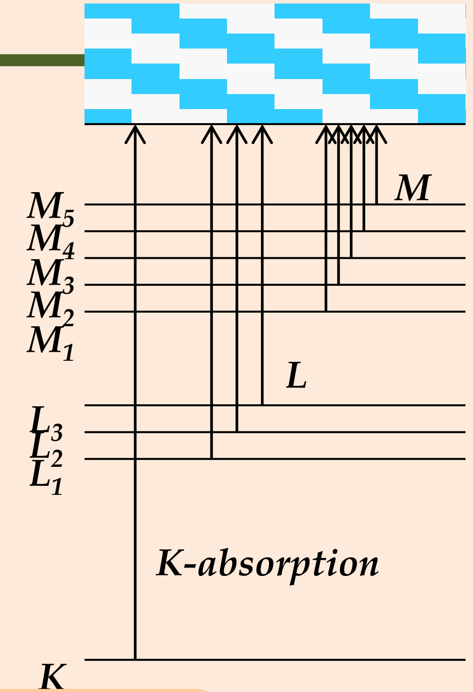
Resonant x-ray scattering technique

Resonant x-ray scattering technique

Atomic scattering factor (ASF): Structure factor of one atom

$$f = f_0(Q) + \underline{f'(E) + if''(E)}$$

Anomalous scattering term



Selective information:
- Element: Absorption energy depends on the atom
- Shell: *K*–, *L*–, *M*–・・・.. edge

Local state around the absorbed atom

- Chemical shift – Charge state
- Tensor of ASF – Strongly reflect the local symmetry
  Orbital state
  Chemical bond
- Spin state

X-ray diffraction → Periodicity

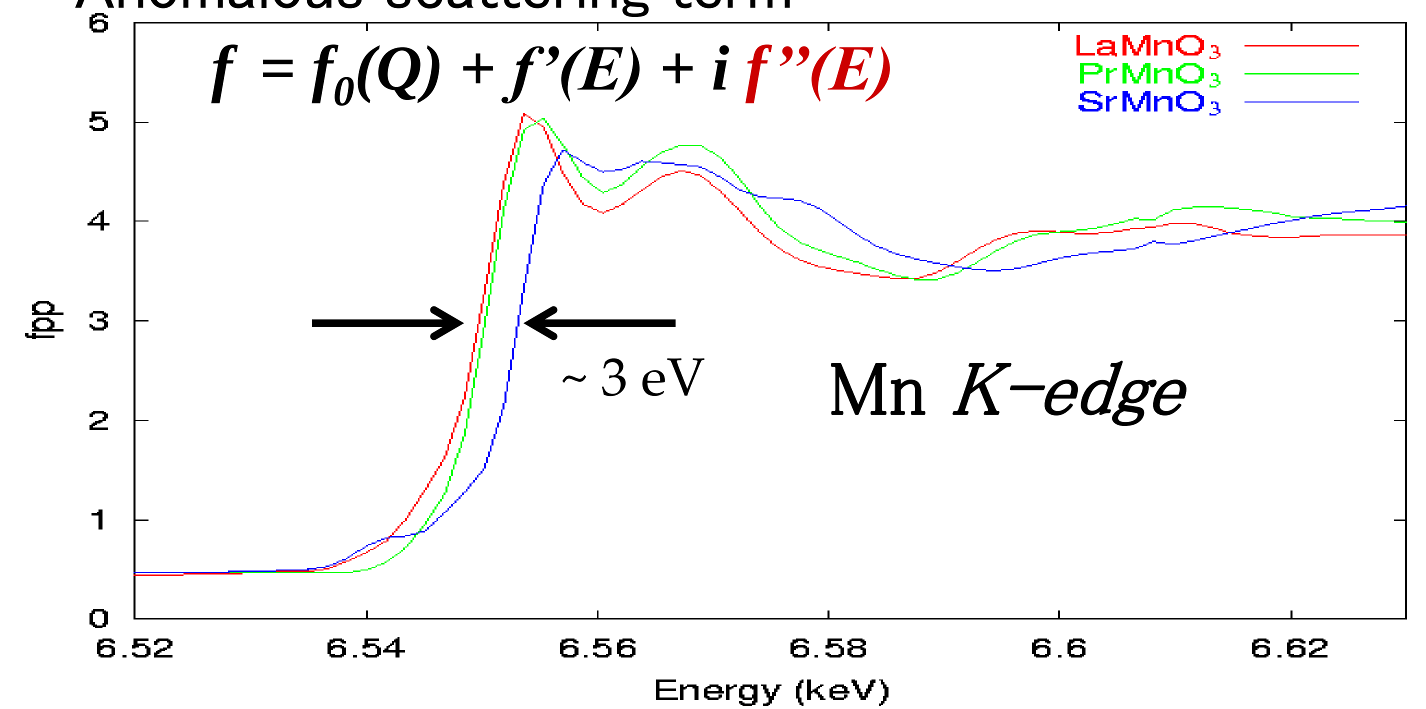
ASF of Mn ion

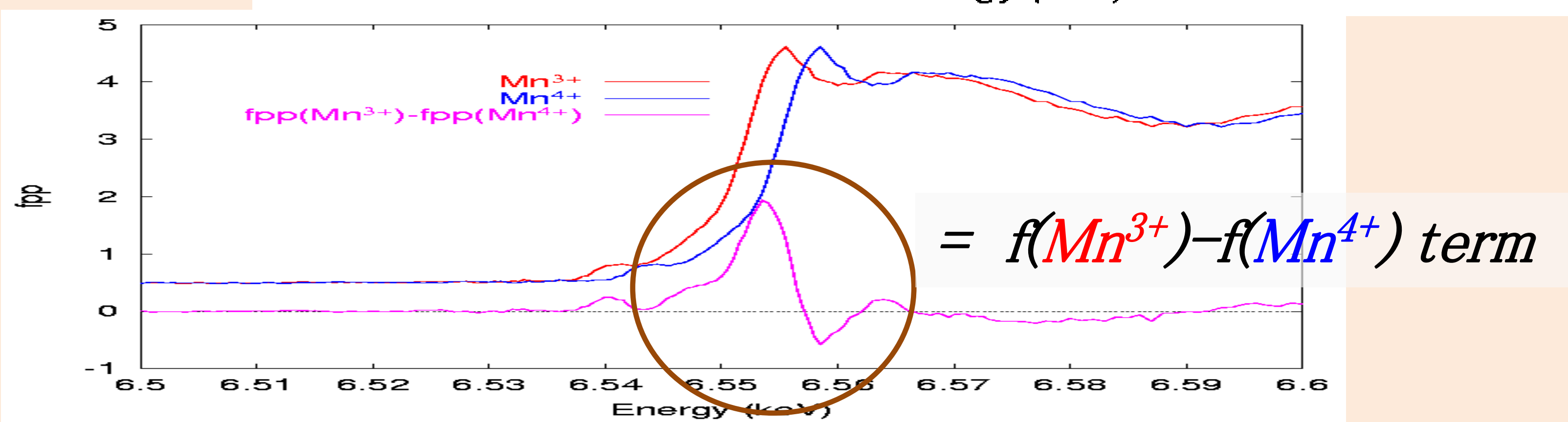
$La^{3+}Mn^{3+}O(O^{2-})_3$

$Pr^{3+}Mn^{3+}O(O^{2-})_3$

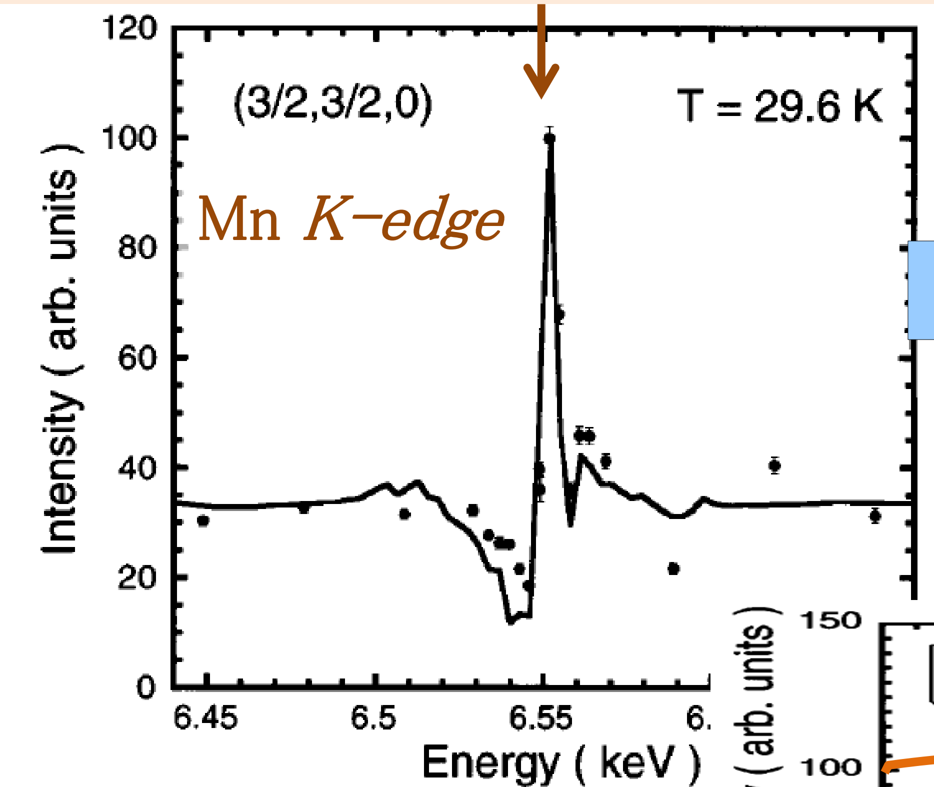
$Sr^{2+}Mn^{4+}O(O^{2-})_3$

Anomalous scattering term



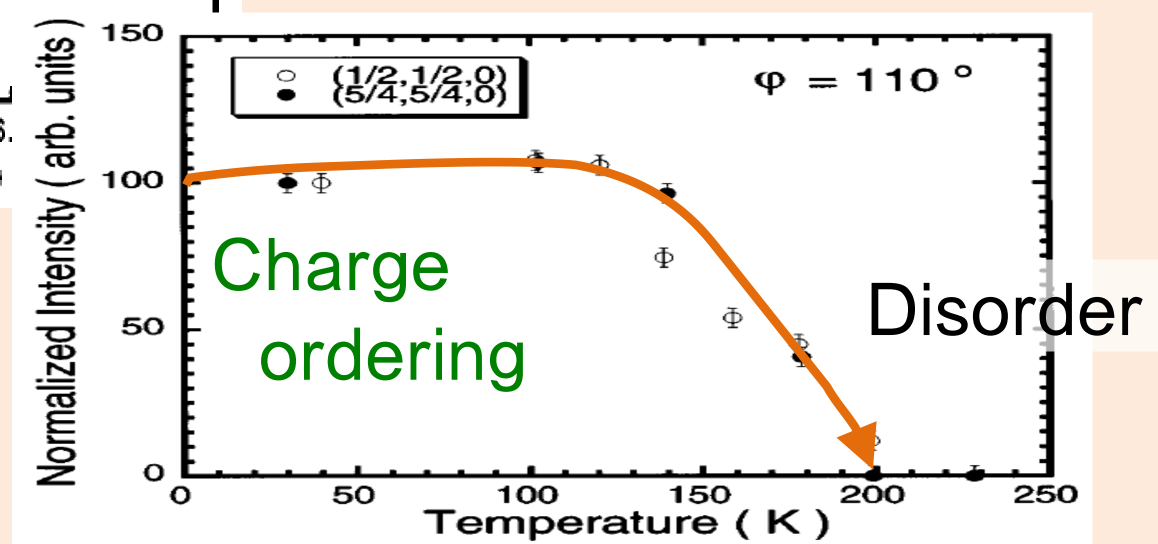


RXS study in $La_{0.5}Sr_{1.5}MnO_4$



Existence of Mn^{3+} *&* Mn^{4+}

Charge ordering



Y. Murakami et al.,
PRL **80** (1998) 1932.

Summary

- Structure and physical properties

- How to determine the structure

  Principle of X-ray diffraction

- Scientific applications

  Dielectic: origins of electric polarization

  CMR: Insulator & Metal phases

Next lecture : **Powder x-ray diffraction**